

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 721 492 B2**

(12) **NEW EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the opposition decision:
19.06.2002 Bulletin 2002/25

(45) Mention of the grant of the patent:
15.09.1999 Bulletin 1999/37

(21) Application number: **94924280.4**

(22) Date of filing: **22.07.1994**

(51) Int Cl.7: **C10L 1/14, C10L 1/18**

(86) International application number:
PCT/EP94/02432

(87) International publication number:
WO 95/03377 (02.02.1995 Gazette 1995/06)

(54) **ADDITIVES AND FUEL COMPOSITIONS**

ZUSÄTZE UND KRAFTSTOFFZUSAMMENSETZUNGEN

ADDITIFS ET COMPOSITONS DE COMBUSTIBLES

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: **22.07.1993 GB 9315205**

(43) Date of publication of application:
17.07.1996 Bulletin 1996/29

(60) Divisional application:
98202903.5 / 0 885 948
98204020.6 / 0 908 507

(73) Proprietor: **Infineum USA L.P.**
Linden, New Jersey 07036 (US)

(72) Inventors:
• **DAVIES, Brian, William**
Oxfordshire OX11 9PD (GB)
• **LOMBARDI, Alessandro**
Oxfordshire OX13 5QF (GB)
• **GOBERDHAN, Dhanesh, Gordon**
Oxford OX2 6DB (GB)

(74) Representative: **Hart, Richard Joseph et al**
Infineum UK Ltd,
Law Department,
Milton Hill,
PO Box 1
Abingdon, Oxfordshire OX13 6BB (GB)

(56) References cited:

EP-A- 0 017 308	EP-A- 0 030 099
EP-A- 0 055 355	EP-A- 0 085 803
EP-A- 0 183 447	EP-A- 0 356 256
EP-A- 0 465 042	EP-A- 0 476 196
WO-A-94/06894	DD-A- 215 803
DE-A- 3 031 344	DE-C- 2 156 425
FR-A- 1 405 551	FR-A- 2 197 062
GB-A- 1 413 323	JP-A- 59 053 594
JP-A- 61 213 292	JP-A- 63 245 488
US-A- 4 365 973	US-A- 5 018 645

Remarks:

The file contains technical information submitted
after the application was filed and not included in this
specification

EP 0 721 492 B2

Description

[0001] This invention relates to the use of additives for improving the cold flow properties of fuel oil, for example distillate petroleum fuel such as middle distillate fuel oil boiling within the range of 110°C to 500°C.

[0002] When fuel oils are subjected to low ambient temperatures, wax may separate out from the fuel and impair the flow properties of the oil. For example, middle distillate fuels contain wax which precipitates at low temperatures to form large waxy crystals which tend to plug the small pore openings of fuel filters. This problem is particularly acute when the fuel is a diesel fuel because the nominal apertures in the fuel filter of diesel engines are typically of diameter between about 5 and 50 micrometers. Additives are known in the art for overcoming the above problem and are called Flow Improvers.

[0003] Such additives may act as wax crystal modifiers when blended with waxy mineral oil by modifying the shape and size of crystals of the wax therein and reducing the adhesive forces between the crystals and between the wax and the oil to permit the oil to remain fluid at a lower temperature than in the absence of the additive.

[0004] Many additives are described in the art for improving the cold-flow properties of oils, for example in the form of oil-soluble addition products or condensates that may be polymeric or monomeric and as described, for example, in US-A-3,048,479; GB-A-1,263,152; US-A-3,961,961; and EP-A-0,261,957. Some of the above additives have been and are used commercially as Cold Flow Improvers.

[0005] The art also describes Cold Flow Improvers as being usable in combination with other additives. For example, GB-A-1,112,808 describes ethylene-vinyl acetate copolymers in combination with rust inhibitors, anti-emulsifying agents, corrosion inhibitors, anti-oxidants, dispersants, dyes, dye-stabilisers, haze-inhibitors, and anti-static additives.

[0006] In this invention, it has surprisingly been found that the cold flow properties of Cold Flow Improvers such as the above-described may be further enhanced by using co-additives not hitherto known in the art to exhibit cold flow improving properties.

[0007] Thus, a first aspect of the invention is the use of a co-additive (A) which comprises an oil-soluble lubricity additive comprising a glycerol monoester of an unsaturated mono-carboxylic acid wherein the acid has from 2 to 50 carbon atoms; said use being in a composition comprising a major proportion of a fuel oil and a minor proportion of component (B) which comprises a cold flow improver additive comprising an ethylene/unsaturated ester copolymer having a number-average molecular weight, as measured by vapour phase osmometry, of 1,000 to 5,000, and being to enhance the cold flow properties of the composition.

[0008] The enhancement of the cold flow performance of component (B) by component (A) according to

this invention can be applied to the blending of additives into a fuel oil. Thus, a second aspect of the invention is a process for blending additives with a fuel oil comprising

- 5 (i) injecting component (B) as defined above into the fuel oil;
- (ii) injecting component (A) as defined above into the fuel oil;
- 10 (iii) measuring the cold flow properties of the fuel oil after the injections of steps (i) and (ii); and
- 15 (iv) adjusting the relative rate of injection of components (B) and (A) and thereby their relative proportions to take account of the results of step (iii) and to provide desired cold flow properties in the fuel oil.
- 20 [0009] The invention also includes a fuel oil composition comprising a major proportion of fuel oil and a combination of:
 - 25 a component (A) which comprises an oil soluble lubricity additive, comprising a glycerol monoester of an unsaturated monocarboxylic acid wherein the acid has from 2 to 50 carbon atoms; and
 - 30 a component (B) which comprises a cold flow improver additive comprising an ethylene/unsaturated ester copolymer having a number-average molecular weight, as measured by vapour phase osmometry, of 1,000 to 5,000, and
 - 35 optionally other additives.
- [0010] The invention further includes an additive concentrate containing component (A) and component (B) as defined above, and optionally other additives.
- 40 [0011] Component (A) may additionally comprise
 - (a) an oil-soluble ashless dispersant/detergent comprising an amine that is acylated with a hydrocarbylcarboxy acylating agent or that is hydrocarbylated or that is hydrocarboxylated;
 - 45 (b) an oil-soluble nitrate or peroxy cetane improver and
 - 50 (c) an oil-soluble petroleum fuel antifoam comprising a silicon-based composition or a polyamine having at least one primary or secondary amino-group, acylated with a carboxylic acylating agent.
- 55 [0012] In the second aspect of this invention, the fuel oil is preferably in the form of a flowing stream wherein step (i) takes place at a first station and step (ii) takes place at a second station, though the first and second

stations may be co-terminous and injection be via a common injector. The process can be automated so that a sensor can carry out step (iii), e.g. by measuring the cold filter plugging point (CFPP), and the information fed via a controller to control injection of one or both of components (B) and (A).

[0013] The invention surprisingly enables less of component (B) to be used to achieve a desired cold flow improvement performance.

[0014] The features of the invention will now be discussed in further detail. Specifications referred to hereinafter are incorporated herein by reference.

[0015] As used in this specification the term "hydrocarbyl" refers to a group having a carbon atom directly attached to the rest of the molecule and having a hydrocarbon or predominantly hydrocarbon character. Examples include hydrocarbon groups, including aliphatic (e.g. alkyl or alkenyl), alicyclic (e.g. cycloalkyl or cycloalkenyl), aromatic, and alicyclic-substituted aromatic, and aromatic-substituted aliphatic and alicyclic groups. Aliphatic groups are advantageously saturated. These groups may contain non-hydrocarbon substituents provided their presence does not alter the predominantly hydrocarbon character of the group. Examples include keto, halo, hydroxy, nitro, cyano, alkoxy and acyl. If the hydrocarbyl group is substituted, a single (mono) substituent is preferred.

[0016] Examples of substituted hydrocarbyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-ketopropyl, ethoxyethyl, and propoxypropyl. The groups may also or alternatively contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include, for example, nitrogen, sulphur, and, preferably, oxygen.

[0017] The acid, alcohol and ester characterising the lubricity additive will now be discussed in further detail as follows.

(i) Acid The acid from which the ester is derived is an unsaturated, straight or branched chain mono carboxylic acid. For example, the acid may be generalised in the formula



where R' represents an alkenyl group having 10 (e.g. 12) to 30 carbon atoms. The alkenyl group may have one or more double bonds, such as 1, 2 or 3. Examples of unsaturated carboxylic acids are those with 10 to 22 carbon atoms such as oleic, elaidic, palmitoleic, petroselic, ricinoleic, eleostearic, linoleic, linolenic, gadoleic, erucic and hypogaecic acids.

(ii) Alcohol The alcohol from which the ester is derived is glycerol.

(iii) The Esters The esters may be used alone or as mixtures of one or more esters and may be com-

posed only of carbon, hydrogen and oxygen. Preferably the ester has a molecular weight of 200 or greater, or has at least 10 carbon atoms, or has both.

[0018] Specific examples are esters prepared from one or more of the above-mentioned unsaturated carboxylic acids, such as glycerol monooleate. Such polyhydric esters may be prepared by esterification as described in the art and/or may be commercially available.

[0019] The ester has more than are free hydroxy groups.

Examples are described in WO-PCT/EP 94/00148.

[0020] Reference is made to additional components as identified above by lower case code letters.

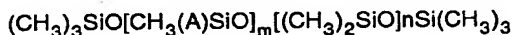
(a) ashless dispersants are dispersants for improving the detergency of fuel oils and leave little or no metal-containing residue on combustion. They are described in numerous patent specifications and include the following:

- polyamines that have been acylated with hydrocarbyl polycarboxy acylating agents (e.g. hydrocarbyl dicarboxylic anhydride) such as alkenyl succinimide polyamines, for example where the alkenyl group is polyisobutylene. Examples are described in EP-A-0,482,253. Also, included are cyclised products of such polyamines such as described in EP-A-0,525,052.
- polyamines that have been hydrocarbylated, e.g. with a polyolefin group such as polyisobutylene. Examples are described in WO-A-91 12302.
- hydrocarbyl ether amines such as alkyl ether monoamines, for example where the hydrocarbyl group has from 6 to 26 carbon atoms (e.g. 8 or 10) and is preferably a methyl branched alkyl such as an oxo-alcohol derivative. The amine may, for example have 2 to 8 carbon atoms. Examples are described in US-A-4,319,987. Other examples are alkoxylated amines such as described in US-A-4,409,000.

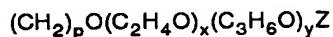
(b) Examples of cetane improvers are organic nitrates, such as nitrate esters containing aliphatic or cyclo-aliphatic groups with up to 30 carbon atoms, preferably saturated groups, and preferably with up to 12 carbon atoms. Examples of such nitrates are methyl, ethyl, propyl, isopropyl, butyl, amyl, hexyl, heptyl, octyl, iso-octyl, 2-ethylhexyl, nonyl, decyl, allyl, cyclo-pentyl, cyclohexyl, methycyclohexyl, cyclodecyl, 2-ethoxyethyl, and 2-(2ethoxyethoxy) ethyl nitrates. Other examples are fuel soluble peroxides, hydroperoxides and peroxy esters.

(c) Examples of anti-foams include siloxane-poly-

oxyalkylene copolymers, for example those described in US-A-3 233 986, which comprise at least one siloxane block containing at least two siloxane groups of the formula $R_2SiO_{0.5(4-b)}$ wherein R represents a halogen atom or an optionally halogenated hydrocarbon group and b represents from 1 to 3, and at least one polyoxylalkylene block containing at least two oxyalkylene groups. Generally, the alkylene groups have 2 or 3 carbon atoms, and usually both ethylenoxy and propyleneoxy groups are present. Advantageously, the copolymer is a polymethylsiloxane-polyoxylalkylene copolymer, preferably of the general formula



in which A represents

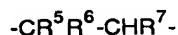


in which Z represents hydrocarbyl, OC(hydrocarbyl) or, preferably, hydrogen, and in which the absolute values of m and n, and their ratios, and the values of p, x, and y, and their ratios, may vary widely but total values advantageously give a weight average molecular weight in the range of from 600 to 25000. The ratio of m:n is advantageously in the range of from 10:1 to 1:20, or the value of n may be zero, and the ratio of x:y is advantageously in the range of from 1:100 to 100:1, preferably 20:80 to 100:1, or one of x or y, but not both, may be zero. Preferred foam inhibitors are those sold under the trade mark TEGOPREN by Th. Goldschmidt AG. Advantageously, the foam inhibitor is present in the fuel in a proportion in the range of from 0.0001 to 0.2%, preferably from 0.005 to 0.02%, by weight. Other anti-foams may be non-silicon containing such as those made by acylating polyamines as described in WO-A-94 06894.

COMPONENT (B)

[0021] Ethylene/unsaturated ester copolymer flow improvers have a polymethylene backbone divided into segments by oxyhydrocarbon side chains.

[0022] More especially, the copolymer may comprise an ethylene copolymer having, in addition to units derived from ethylene, units of the formula



wherein R^6 represents hydrogen or a methyl group; R^5 represents a $-OOCR^8$ or $-COOR^8$ group wherein R^8 represents hydrogen or a C_1 to C_{28} , preferably C_1 to C_9 , straight or branched chain alkyl group, provided that R^8

does not represent hydrogen when R^5 represents $-COOR^8$; and R^7 is hydrogen or $-COOR^8$.

[0023] These comprise a copolymer of ethylene with an ethylenically unsaturated ester, or derivatives thereof. An example is a copolymer of ethylene with an ester of an unsaturated carboxylic acid, but the ester is preferably one of an unsaturated alcohol with a saturated carboxylic acid. An ethylene-vinyl ester copolymer is advantageous; an ethylene-vinyl acetate, ethylene vinyl propionate, ethylene-vinyl hexanoate, or ethylene-vinyl octanoate copolymer is preferred. Preferably, the copolymers contain from 1 to 25, e.g. 1 to 20 mole % of the vinyl ester, more preferably from 3 to 17 mole % vinyl ester. They may also be in the form of mixtures of two copolymers such as those described in US-A3,961,916. The number average molecular weight, as measured by vapour phase osmometry, of the copolymer is 1,000 to 5,000. If desired, the copolymers may be derived from additional comonomers, e.g. they may be terpolymers or tetrapolymers or higher polymers, for example where the additional comonomer is isobutylene or diisobutylene.

[0024] The copolymers may be made by direct polymerisation of comonomers. Such copolymers may also be made by transesterification, or by hydrolysis and reesterification, of an ethylene unsaturated ester copolymer to give a different ethylene unsaturated ester copolymer. For example, ethylene vinyl hexanoate and ethylene vinyl octanoate copolymers may be made in this way, e.g. from an ethylene vinyl acetate copolymer.

[0025] Component (B) may be used with co-components such as one or more of the following:

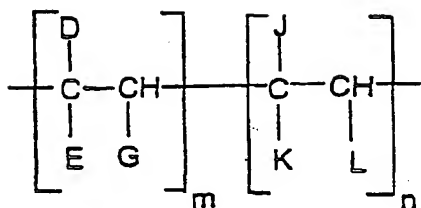
Comb Polymers

[0026] Comb polymers are discussed in "Comb-Like Polymers. Structure and Properties", N. A. Plate and V. P. Shibaev, J. Poly. Sci. Macromolecular Revs., 8, p 117 to 253 (1974).

[0027] Generally, comb polymers have one or more long chain branches such as hydrocarbyl branches, such as oxyhydrocarbyl branches, having from 10 to 30 carbon atoms, pendant from a polymer backbone, said branch or branches being bonded directly or indirectly to the backbone. Examples of indirect bonding include bonding via interposed atoms or groups, which bonding can include covalent and/or electrovalent bonding such as in a salt.

[0028] Advantageously, the comb polymer is a homopolymer having, or a copolymer at least 25 and preferably at least 40, more preferably at least 50, molar per cent of the units of which have, side chains containing at least 6, and preferably at least 10, atoms, selected from for example carbon, nitrogen and oxygen, in a linear chain.

[0029] As examples of preferred comb polymers there may be mentioned those containing units of the general formula



where

- D = R¹¹, COOR¹¹, OCOR¹¹, R¹²COOR¹¹ or OR¹¹
 E = H, CH₃, D or R¹²
 G = H or D
 J = H, R¹², R¹²COOR¹¹, or an aryl or heterocyclic group
 K = H, COOR¹², OCOR¹², OR¹² or COOH
 L = H, R¹², COOR¹², OCOR¹² or aryl
 R¹¹ ≥ C₁₀ hydrocarbyl
 R¹² ≥ C₁ hydrocarbyl

and m and n represent mole ratios, their sum being 1 and m being finite and being up to and including 1 and n being from zero to less than 1, preferably m being within the range of from 1.0 to 0.4, n being in the range of from 0 to 0.6. R¹¹ advantageously represents a hydrocarbyl group with from 10 to 30 carbon atoms, and R¹² advantageously represents a hydrocarbyl group with from 1 to 30 carbon atoms.

[0030] The comb polymer may contain units derived from other monomers if desired or required. It is within the scope of the invention to include two or more different comb copolymers.

[0031] These comb polymers may be copolymers of maleic anhydride or fumaric acid and another ethylenically unsaturated monomer, e.g. an α-olefin or an unsaturated ester, for example, vinyl acetate. It is preferred but not essential that equimolar amounts of the comonomers be used although molar proportions in the range of 2 to 1 and 1 to 2 are suitable. Examples of olefins that may be copolymerized with e.g. maleic anhydride, include 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene.

[0032] The copolymer may be esterified by any suitable technique and although preferred it is not essential that the maleic anhydride or fumaric acid be at least 50% esterified. Examples of alcohols which may be used include n-decan-1-ol, n-dodecan-1-ol, n-tetradecan-1-ol, n-hexadecan-1-ol, and n-octadecan-1-ol. The alcohols may also include up to one methyl branch per chain, for example, 1-methylpentadecan-1-ol, 2-methyltridecan-1-ol. The alcohol may be a mixture of normal and single methyl branched alcohols. It is preferred to use pure alcohols rather than the commercially available alcohol mixtures but if mixtures are used the R¹² refers to the average number of carbon atoms in the alkyl group; if alcohols that contain a branch at the 1 or 2 positions are

used R¹² refers to the straight chain backbone segment of the alcohol.

[0033] These comb polymers may especially be fumarate or itaconate polymers and copolymers such as for example those described in European Patent Applications EP-A-153 176, EP-A-153 177 and EP-A-225 688, and WO-A-91 16407.

[0034] Particularly preferred fumarate comb polymers are copolymers of alkyl fumarates and vinyl acetate, in which the alkyl groups have from 12 to 20 carbon atoms, more especially polymers in which the alkyl groups have 14 carbon atoms or in which the alkyl groups are a mixture of C₁₄/C₁₆ alkyl groups, made, for example, by solution copolymerizing an equimolar mixture of fumaric acid and vinyl acetate and reacting the resulting copolymer with the alcohol or mixture of alcohols, which are preferably straight chain alcohols. When the mixture is used it is advantageously a 1:1 by weight mixture of normal C₁₄ and C₁₆ alcohols. Furthermore, mixtures of the C₁₄ ester with the mixed C₁₄/C₁₆ ester may advantageously be used. In such mixtures, the ratio of C₁₄ to C₁₄/C₁₆ is advantageously in the range of from 1:1 to 4:1, preferably 2:1 to 7:2, and most preferably about 3:1, by weight. The particularly preferred fumarate comb polymers may, for example, have a number average molecular weight in the range of 1,000 to 100,000, preferably 1,000 to 30,000, as measured by Vapour Phase Osmometry (VPO).

[0035] Other suitable comb polymers are the polymers and copolymers of α-olefins and esterified copolymers of styrene and maleic anhydride, and esterified copolymers of styrene and fumaric acid; mixtures of two or more comb polymers may be used in accordance with the invention and, as indicated above, such use may be advantageous.

[0036] Other examples of comb polymers are hydrocarbon polymers such as copolymers of ethylene and at least one α-olefin, preferably the α-olefin having at most 20 carbon atoms, examples being n-decene-1 and n-dodecene-1. Preferably, the number average molecular weight of such a copolymer is at least 30,000. The hydrocarbon copolymers may be prepared by methods known in the art, for example using a Ziegler type catalyst.

Linear Group Compounds

[0037] Such compounds comprise a compound in which at least one substantially linear alkyl group having 10 to 30 carbon atoms is connected to a non-polymeric organic residue to provide at least one linear chain of atoms that includes the carbon atoms of said alkyl groups and one or more non-terminal oxygen atoms.

[0038] By "substantially linear" is meant that the alkyl group is preferably straight chain, but that essentially straight chain alkyl groups having a small degree of branching such as in the form of a single methyl group may be used.

[0039] Preferably, the compound has a least two of said alkyl groups when the linear chain may include the carbon atoms of more than one of said alkyl groups. When the compound has at least three of said alkyl groups, there may be more than one of such linear chains, which chains may overlap. The linear chain or chains may provide part of a linking group between any two such alkyl groups in the compound.

[0040] The oxygen atom or atoms are preferably directly interposed between carbon atoms in the chain and may, for example, be provided in the form of a mono- or poly-oxyalkylene group, said oxyalkylene group preferably having 2 to 4 carbon atoms, examples being oxyethylene and oxypropylene.

[0041] As indicated the chain or chains include carbon and oxygen atoms. They may also include other heteroatoms such as nitrogen atoms.

[0042] The compound may be an ester where the alkyl groups are connected to the remainder of the compound as -O-CO n alkyl, or -CO-O n alkyl groups, in the former the alkyl groups being derived from an acid and the remainder of the compound being derived from a polyhydric alcohol and in the latter the alkyl groups being derived from an alcohol and the remainder of the compound being derived from a polycarboxylic acid. Also, the compound may be an ester where the alkyl groups are connected to the remainder of the compound as -O-n-alkyl groups. The compound may be both an ester and an ether or it may contain different ester groups.

[0043] Examples include polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof, particularly those containing at least one, preferably at least two, C₁₀ to C₃₀ linear alkyl groups and a polyoxyalkylene glycol group of molecular weight up to 5,000, preferably 200 to 5,000, the alkylene group in said polyoxyalkylene glycol containing from 1 to 4 carbon atoms, as described in EP-A-61 895 and in US-A-4,491,455.

[0044] The preferred esters, ethers or ester/ethers which may be used may be structurally depicted by the formula



[0045] where R²³ and R²⁴ are the same or different and may be

- (a) n-alkyl-
- (b) n-alkyl-CO-
- (c) n-alkyl-OCO-(CH₂)_n-
- (d) n-alkyl-OCO-(CH₂)_nCO-

n being, for example, 1 to 34, the alkyl group being linear and containing from 10 to 30 carbon atoms, and B representing the polyalkylene segment of the glycol in which the alkylene group has from 1 to 4 carbon atoms, for example, polyoxymethylene, polyoxyethylene or polyoxytrimethylene moiety which is substantially linear;

some degree of branching with lower alkyl side chains (such as in polyoxypropylene glycol) may be tolerated but it is preferred that the glycol should be substantially linear. B may also contain nitrogen.

[0046] Suitable glycols generally are substantially linear polyethylene glycols (PEG) and polypropylene glycols (PPG) having a molecular weight of about 100 to 5,000, preferably about 200 to 2,000. Esters are preferred and fatty acids containing from 10 to 30 carbon atoms are useful for reacting with the glycols to form the ester additives, it being preferred to use C₁₈ to C₂₄ fatty acid, especially behenic acid. The esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols.

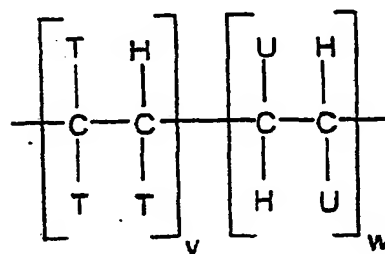
[0047] Polyoxyalkylene diesters, diethers, ether/esters and mixtures thereof are suitable as additives, diesters being preferred when the petroleum based component is a narrow boiling distillate, when minor amounts of monoethers and monoesters (which are often formed in the manufacturing process) may also be present. It is important for active performance that a major amount of the dialkyl compound is present. In particular, stearic or behenic diesters of polyethylene glycol, polypropylene glycol or polyethylene/polypropylene glycol mixtures are preferred.

[0048] Examples of other compounds in this general category are those described in Japanese Patent Publication Nos. 2-51477 and 3-34790, and EP-A-117,108 and EP-A-326,356, and cyclic esterified ethoxylates such as described EP-A-356,256.

Hydrocarbon Polymers

[0049] Examples are those represented by the following general formula

[0050]



where

T = H or R¹

U = H, T or aryl

R¹ = C₁₋₃₀ hydrocarbyl

and v and w represent mole ratios, v being within the range 1.0 to 0.0, w being within the range 0.0 to 1.0.

[0051] These polymers may be made directly from

ethylenically unsaturated monomers or indirectly by hydrogenating the polymer made from monomers such as isoprene and butadiene.

[0052] Preferred hydrocarbon polymers are copolymers of ethylene and at least one α -olefin, having a number average molecular weight of at least 30,000. Preferably the α -olefin has at most 20 carbon atoms. Examples of such olefins are propylene, 1-butene, isobutene, n-octane-1, isooctene-1, n-decene-1, and n-dodecene-1. The copolymer may also comprise small amounts, e.g. up to 10% by weight of other copolymerizable monomers, for example olefins other than α -olefins, and non-conjugated dienes. The preferred copolymer is an ethylene-propylene copolymer. It is within the scope of the invention to include two or more different ethylene- α -olefin copolymers of this type.

[0053] The number average molecular weight of the ethylene- α -olefin copolymer is, as indicated above, at least 30,000, as measured by gel permeation chromatography (GPC) relative to polystyrene standards, advantageously at least 60,000 and preferably at least 80,000. Functionally no upper limit arises but difficulties of mixing result from increased viscosity at molecular weights above about 150,000, and preferred molecular weight ranges are from 60,000 and 80,000 to 120,000.

[0054] Advantageously, the copolymer has a molar ethylene content between 50 and 85 per cent. More advantageously, the ethylene content is within the range of from 57 to 80%, and preferably it is in the range from 58 to 73%; more preferably from 62 to 71%, and most preferably 65 to 70%.

[0055] Preferred ethylene- α -olefin copolymers are ethylene-propylene copolymers with a molar ethylene content of from 62 to 71% and a number average molecular weight in the range 60,000 to 120,000, especially preferred copolymers are ethylene-propylene copolymers with an ethylene content of from 62 to 71% and a molecular weight from 80,000 to 100,000.

[0056] The copolymers may be prepared by any of the methods known in the art, for example using a Ziegler type catalyst. Advantageously, the polymers are substantially amorphous, since highly crystalline polymers are relatively insoluble in fuel oil at low temperatures.

[0057] The additive composition may also comprise a further ethylene- α -olefin copolymer, advantageously with a number average molecular weight of at most 7500, advantageously from 1,000 to 6,000, and preferably from 2,000 to 5,000, as measured by vapour phase osmometry. Appropriate α -olefins are as given above, or styrene, with propylene again being preferred. Advantageously the ethylene content is from 60 to 77 molar per cent although for ethylene-propylene copolymers up to 86 molar per cent ethylene may be employed with advantage.

Examples of hydrocarbon polymers are described in WO-A-9 111 488.

Polar Compounds

[0058] Such compounds comprise an oil-soluble polar nitrogen compound carrying one or more, preferably two or more, substituents of the formula $=NR^1$, where R^1 represents a hydrocarbonyl group containing B to 40 atoms, which substituent or one or more of which substituents may be in the form of a cation derived therefrom. The oil-soluble polar nitrogen compound is either ionic or non-ionic and is capable of acting as a wax crystal growth inhibitor in fuels. It comprises for example one or more of the compounds (i) to (iii) as follows:

[0059] (i) An amine salt and/or amide formed by reacting at least one molar proportion of a hydrocarbonyl substituted amine with a molar proportion of a hydrocarbonyl acid having 1 to 4 carboxylic acid groups or its anhydride, the substituent(s) of formula $=NR^1$ being of the formula $-NR^1 R^2$ where R^1 is defined as above and R^2 represents hydrogen or R^1 , provided that R^1 and R^2 may be the same or different, said substituents constituting part of the amine salt and/or amide groups of the compound.

[0060] Ester/amides may be used containing 30 to 300, preferably 50 to 150 total carbon atoms. These nitrogen compounds are described in US-A-4 211 534. Suitable amines are usually long chain C_{12} - C_{40} primary, secondary, tertiary or quaternary amines or mixtures thereof but shorter chain amines may be used provided the resulting nitrogen compound is oil soluble and therefore normally contains about 30 to 300 total carbon atoms. The nitrogen compound preferably contains at least one straight chain C_8 to C_{40} , preferably C_{14} to C_{24} , alkyl segment.

[0061] Suitable amines include primary, secondary, tertiary or quaternary, but preferably are secondary. Tertiary and quaternary amines can only form amine salts. Examples of amines include tetradecyl amine, cocoamine, and hydrogenated tallow amine. Examples of secondary amines include dioctadecyl amine and methyl-behenyl amine. Amine mixtures are also suitable such as those derived from natural materials. A preferred amine is a secondary hydrogenated tallow amine of the formula $HNR^1 R^2$ wherein R^1 and R^2 are alkyl groups derived from hydrogenated tallow fat composed of approximately 4% C_{14} , 31% C_{16} , 59% C_{18} .

[0062] Examples of suitable carboxylic acids and their anhydrides for preparing the nitrogen compounds include cyclohexane 1,2 dicarboxylic acid, cyclohexene 1,2 dicarboxylic acid, cyclopentane 1,2 dicarboxylic acid and naphthalene dicarboxylic acid, and 1,4-dicarboxylic acids including dialkyl spirobis lactone. Generally, these acids have about 5-13 carbon atoms in the cyclic moiety. Preferred acids useful in the present invention are benzene dicarboxylic acids such as phthalic acid, isophthalic acid, and terephthalic acid. Phthalic acid or its anhydride is particularly preferred. The particularly preferred compound is the amide-amine salt formed by reacting 1 molar portion of phthalic anhydride with 2 molar por-

tions of dihydrogenated tallow amine. Another preferred compound is the diamide formed by dehydrating this amide-amine salt.

[0063] Other examples are long chain alkyl or alkylene substituted dicarboxylic acid derivatives such as amine salts of monoamides of substituted succinic acids, examples of which are known in the art and described in US-A-4 147 520, for example. Suitable amines may be those described above.

Other examples are condensates such as described in EP-A-327,423.

[0064] (ii) A chemical compound comprising or including a cyclic ring system, the compound carrying at least two substituents of the general formula (I) below on the ring system



where A is an aliphatic hydrocarbyl group that is optionally interrupted by one or more hetero atoms and that is straight chain or branched, and R¹ and R² are the same or different and each is independently a hydrocarbyl group containing 9 to 40 carbon atoms optionally interrupted by one or more hetero atoms, the substituents being the same or different and the compound optionally being in the form of a salt thereof.

[0065] Preferably, A has from 1 to 20 carbon atoms and is preferably a methylene or polymethylene group.

[0066] As used in this specification the term "hydrocarbyl" refers to a group having a carbon atom directly attached to the rest of the molecule and having a hydrocarbon or predominantly hydrocarbon character. Examples include hydrocarbon groups, including aliphatic (e.g. alkyl or alkenyl), alicyclic (e.g. cycloalkyl or cycloalkenyl), aromatic, and alicyclic-substituted aromatic, and aromatic-substituted aliphatic and alicyclic groups. Aliphatic groups are advantageously saturated. These groups may contain non-hydrocarbon substituents provided their presence does not alter the predominantly hydrocarbon character of the group. Examples include keto, halo, hydroxy, nitro, cyano, alkoxy and acyl. If the hydrocarbyl group is substituted, a single (mono) substituent is preferred.

[0067] Examples of substituted hydrocarbyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-ketopropyl, ethoxyethyl, and propoxypropyl. The groups may also or alternatively contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include, for example, nitrogen, sulphur, and, preferably, oxygen.

[0068] The cyclic ring system may include homocyclic such as hexane, pentane and isoparaffins, and includes mixtures of the above. The carrier liquid must, of course, be selected having regard to its compatibility with the additive and with the fuel.

[0069] The additives of the invention may be incorpo-

rated into bulk oil by other methods such as those known in the art. If others are required, they may be incorporated into the bulk oil at the same time as the additives of the invention or at a different time. Examples of other additives include antioxidants, corrosion inhibitors, de-hazers, metal deactivators, cosolvents, package compatibilisers, reodorants, antistatic additives (conductivity improvers), biocides, dyes, smoke reducers, catalyst life enhancers, power boosters, additives for fuel economy, demulsifiers, and spray modifiers.

[0070] The following compounds can be used in the invention.

Additives

[0071]

- B1: an ethylene-vinyl acetate copolymer of number average molecular weight 3,300 as measured by Gel Permeation Chromatography (GPC) and containing about 36% by weight of vinyl acetate.
- B2: an ethylene-vinyl acetate copolymer of number average molecular weight 5,000 as measured by GPC and containing about 13.5% by weight of vinyl acetate.
- B3: a mixture of additives B1 and B2 in the weight: weight ratio (B1:B2) of 3:1.
- C: a N,N-dialkylammonium salt of 2-N¹,N¹-dialkylamido benzoate, being the reaction product of reacting one mole of phthalic anhydride with two moles of dihydrogenated tallow amine to form a half amide/half amine salt.

Tests

[0072] The following tests assess the effectiveness of the additives tested as filterability improvers in distillate fuels.

Simulated Filter Plugging Point (SFPP)

[0073] The test was carried out by the procedure substantially as described in EP-A-0,403,097 and is a variation of the CFPP test.

The Cold Filter Plugging Point Test (or CFPP Test)

[0074] The test which is carried out by the procedure described in detail in "Journal of the Institute of Petroleum", Volume 52, Number 510, June 1966, pp. 173-285, is designed to correlate with the cold flow of a middle distillate in automotive diesels.

[0075] In brief, a sample of the oil to be tested (40 ml) is cooled in a bath which is maintained at about -34°C to give non-linear cooling at about 1°C/min. Periodically (at each one degree centigrade starting from above the cloud point), the cooled oil tested for its ability to flow through a fine screen in a prescribed time-period using

a test device which is a pipette to whose lower end is attached an inverted funnel which is positioned below the surface of the oil to be tested. Stretched across the mouth of the funnel is a 350 mesh screen having an area defined by a 12 millimetre diameter. The periodic tests are each initiated by applying a vacuum to the upper end of the pipette whereby oil is drawn through the screen up into the pipette to a mark indicating 20 ml of oil. After each successful passage, the oil is returned immediately to the CFPP tube. The test is repeated with each one degree drop in temperature until the oil fails to fill the pipette within 60 seconds, the temperature at which failure occurs being reported as the CFPP temperature.

[0076] The additive combinations of the invention may also be effective in reducing the tendency of wax in the fuel to settle (i.e. they may be wax anti-settling additives) and may exhibit activity in slow cooling tests such as the Extended Programmed Cooling Test (XPCT) which is known in the art.

[0077] Components BX and BY:

BX: B2 (56 ppm) B1 (169 ppm) 7 (75 ppm) C (75 ppm)

BY: B2 (50 ppm) 3 (100 ppm) 6 (100 ppm) C (100 ppm) 5 (200 ppm)

[0078] The concentrations of the constituents of Components BX and BY in the fuels are given in parentheses as weight per cent of fuel. The constituents, identified by reference numbers 3 and 5 to 7 above, are as follows (additional to constituents already defined herein)

[0079] 3: an ethylene-vinyl acetate copolymer of number average molecular weight of 3,300 as measured by GPC and containing 36% by weight of vinyl acetate.

[0080] 5: an itaconate polymer of number average molecular weight about 4000 as measured by GPC prepared by polymerising a monomer in cyclohexane solvent using a free radical catalyst, the monomer containing linear alkyl groups of 18 carbon atoms.

[0081] 6: a copolymer of styrene and esterified fumaric acid wherein the alkyl groups have 14 carbon atoms, the copolymer having a number average molecular weight of 15000 as measured by GPC and proportions of styrene and esterified fumaric acid in the ratio of 1:1 (mole:mole).

[0082] 7: a fumarate ester vinyl acetate copolymer of number average molecular weight of about 20,000 as measured by GPC, the fumarate ester containing linear alkyl groups of 12-14 carbon atoms.

Claims

1. The use of a co-additive (A) which comprises an oil soluble lubricity additive comprising a glycerol monoester of an unsaturated monocarboxylic acid,

wherein the acid has from 2 to 50 carbon atoms; said use being in a composition comprising a major proportion of a fuel oil and a minor proportion of component (B) which comprises a cold flow improver additive comprising an ethylene/unsaturated ester copolymer having a number-average molecular weight, as measured by vapour phase osmometry, of 1,000 to 5,000, and being to enhance the cold flow properties of the composition.

2. The use of claim 1 wherein the lubricity additive comprises the ester of a monocarboxylic acid of the formula:



wherein R' represents an alkenyl group having 10 to 30 carbon atoms.

3. The use of claim 2 wherein the alkenyl group has 1, 2 or 3 double bonds.
4. The use of any of the preceding claims wherein the acid is oleic, elaidic, palmitoleic, petroselic, ricinoleic, eleostearic, linoleic, linolenic, gadoleic, erucic or hypogaeic acid.
5. The use of any of the preceding claims wherein the glycerol monoester is glycerol mono-oleate.
6. The use of any of the preceding claims wherein component (B) comprises an ethylene/unsaturated ester copolymer.
7. The use of claim 6 wherein the unsaturated ester is of an unsaturated alcohol with a saturated carboxylic acid.
8. The use of any of the preceding claims additionally comprising, as a co-additive, an oil-soluble polar nitrogen compound carrying one or more substituents of the formula NR^1 , wherein R^1 represents a hydrocarbyl group containing 8 to 40 carbon atoms, which substituents or one or more of which substituents is optionally in the form of a cation derived therefrom.
9. The use of any of the preceding claims wherein the fuel oil is a middle distillate fuel oil.
10. The use of any of the preceding claims wherein the total concentration of components (A) and (B) in the fuel oil is in the range 25 to 500ppm of active ingredient by weight per weight of fuel oil.
11. A fuel oil composition comprising a major proportion of a fuel oil and a combination of:

a component (A) which comprises an oil soluble lubricity additive comprising a glycerol monoester of an unsaturated monocarboxylic acid, wherein the acid has from 2 to 50 carbon atoms; and

a component (B) which comprises a cold flow improver additive comprising an ethylene/unsaturated ester copolymer having a number-average molecular weight, as measured by vapour phase osmometry, of 1,000 to 5,000; and

optionally other additives.

12. An additive concentrate containing:

a component (A) which comprises an oil soluble lubricity additive comprising a glycerol monoester of an unsaturated monocarboxylic acid, wherein the acid has from 2 to 50 carbon atoms; and

a component (B) which comprises a cold flow improver additive comprising an ethylene/unsaturated ester copolymer having a number-average molecular weight, as measured by vapour phase osmometry, of 1,000 to 5,000; and

optionally other additives.

13. The composition of claim 11 or claim 12 wherein the lubricity additive comprises the ester of a monocarboxylic acid of the formula:



wherein R' represents an alkenyl group having 10 to 30 carbon atoms.

14. The composition of claim 13 wherein the alkenyl group has 1, 2 or 3 double bonds.

15. The composition of any of claims 11 to 14 wherein the acid is oleic, elaidic, palmitoleic, petroselic, ricinoleic, eleostearic, linoleic linolenic, gadoleic, erucic or hypogaeic acid.

16. The composition of any of claims 11 to 15 wherein the glycerol monoester is glycerol mono-oleate.

17. The composition of any of claims 11 to 16 wherein component (B) comprises an ethylene/unsaturated ester copolymer wherein the unsaturated ester is of an unsaturated alcohol with a saturated carboxylic acid.

18. The composition of any of claims 11 to 17 addition-

ally comprising, as a co-additive, a oil-soluble polar nitrogen compound carrying one or more substituents of the formula $-N R^1 -$, wherein R^1 represents a hydrocarbonyl group containing 8 to 40 carbon atoms, which substituents or one or more of which substituents is optionally in the form of a carbon derived therefrom.

19. The composition of claim 11, or of any of claims 13 to 18 when dependent on claim 11, wherein the fuel oil is middle distillate fuel oil.

20. The composition of claim 11, or of any of claims 13 to 19 when dependent on claim 11, wherein the total concentration of components (A) and (B) in the fuel oil is in the range 25 to 500ppm of active ingredient by weight per weight of fuel oil.

21. A process for blending additives with a fuel oil comprising:

(i) injecting component (B) as defined in claim 1 into the fuel oil;

(ii) injecting component (A) as defined in claim 1 into the fuel oil;

(iii) measuring the cold flow properties of the fuel oil after the injections of steps (i) and (ii); and

(iv) adjusting the relative rates of injection of component (B) and (A) and thereby their relative proportions to take account of the results of step (iii) and to provide desired cold flow properties in the fuel oil.

22. The process of claim 21 wherein the fuel oil comprises a flowing stream thereof, step (i) taking place at a first station and step (ii) taking place at a second station.

23. The process of claim 21 or 22 wherein a sensor carries out step (iii) and information is fed via a controller to control injection of one or both of components (B) and (A).

Patentansprüche

- Verwendung von Coadditiv (A), das ein öllösliches Schmierfähigkeitsadditiv umfasst, das einen Glycerinmonoester von ungesättigter Monocarbonsäure umfasst, bei dem die Säure 2 bis 50 Kohlenstoffatome aufweist, wobei die Verwendung in einer Zusammensetzung erfolgt, die einen größeren Anteil Treib- oder Brennstofföl und einen geringeren Anteil Komponente (B) umfasst, die ein Kaltfließver-

bessereradditiv umfasst, das ein Ethylen/ungesättigter Ester-Copolymer mit einem durchschnittlichen Molekulargewicht (Zahlenmittel), gemessen durch Dampfphasenosmometrie, von 1000 bis 5000 umfasst und die Kaltfließigenschaften der Zusammensetzung verbessert.

2. Verwendung nach Anspruch 1, bei der das Schmierfähigkeitsadditiv den Ester einer Monocarbonsäure mit der Formel



umfasst, in der R' eine Alkenylgruppe mit 10 bis 30 Kohlenstoffatomen bedeutet.

3. Verwendung nach Anspruch 2, bei der die Alkenylgruppe 1, 2 oder 3 Doppelbindungen aufweist.

4. Verwendung nach einem der vorhergehenden Ansprüche, bei der die Säure Öl-, Elaidin-, Palmitolein-, Petroselin-, Ricinol-, Eleostearin-, Linol-, Linolen-, Gadolein-, Erucaoder Hypogäasäure ist.

5. Verwendung nach einem der vorhergehenden Ansprüche, bei der der Glycerinmonoester Glycerinmonooleat ist.

6. Verwendung nach einem der vorhergehenden Ansprüche, bei der Komponente (B) ein Ethylen/ungesättigter Ester-Copolymer umfasst.

7. Verwendung nach Anspruch 6, bei der der ungesättigte Ester von ungesättigtem Alkohol mit gesättigter Carbonsäure ist.

8. Verwendung nach einem der vorhergehenden Ansprüche, die zusätzlich als Coadditiv eine öllösliche polare Stickstoffverbindung mit einem oder mehreren Substituenten mit der Formel $-NR^1-$ umfasst, in der R^1 eine Kohlenwasserstoffgruppe mit 8 bis 40 Kohlenstoffatomen bedeutet, wobei die Substituenten oder einer oder mehrere der Substituenten gegebenenfalls in Form eines davon abgeleiteten Kations vorliegt.

9. Verwendung nach einem der vorhergehenden Ansprüche, bei der das Treib- oder Brennstofföl Mitteldestillattreib- oder -brennstofföl ist.

10. Verwendung nach einem der vorhergehenden Ansprüche, bei der die Gesamtkonzentration der Komponenten (A) und (B) in dem Treib- oder Brennstofföl im Bereich von 25 bis 500 Gew.ppm aktiver Bestandteil je Gewichtsteil Treib- oder Brennstofföl liegt.

11. Brennstoffölszusammensetzung, die einen größeren Anteil Treib- oder Brennstofföl und eine Kombination aus

Komponente (A), die ein öllösliches Schmierfähigkeitsadditiv umfasst, das einen Glycerinmonoester von ungesättigter Monocarbonsäure umfasst, wobei die Säure 2 bis 50 Kohlenstoffatome aufweist, und

Komponente (B), die ein Kaltfließverbessereradditiv umfasst, das Ethylen/ungesättigter Ester-Copolymer mit einem durchschnittlichen Molekulargewicht (Zahlenmittel), gemessen mittels Dampfphasenosmometrie, von 1000 bis 5000 umfasst,

und gegebenenfalls anderen Additiven umfasst.

12. Additivkonzentrat, das

Komponente (A), die ein öllösliches Schmierfähigkeitsadditiv umfasst, das einen Glycerinmonoester von ungesättigter Monocarbonsäure umfasst, wobei die Säure 2 bis 50 Kohlenstoffatome aufweist, und

Komponente (B), die ein Kaltfließverbessereradditiv umfasst, das Ethylen/ungesättigter Ester-Copolymer mit einem durchschnittlichen Molekulargewicht (Zahlenmittel), gemessen mittels Dampfphasenosmometrie, von 1000 bis 5000 umfasst,

und gegebenenfalls andere Additive enthält.

13. Zusammensetzung nach Anspruch 11 oder Anspruch 12, bei der das Schmierfähigkeitsadditiv den Ester einer Monocarbonsäure mit der Formel



umfasst, in der R' eine Alkenylgruppe mit 10 bis 30 Kohlenstoffatomen bedeutet.

14. Zusammensetzung nach Anspruch 13, bei der die Alkenylgruppe 1, 2 oder 3 Doppelbindungen aufweist.

15. Zusammensetzung nach einem der Ansprüche 11 bis 14, bei der die Säure Öl-, Elaidin-, Palmitolein-, Petroselin-, Ricinol-, Eleostearin-, Linol-, Linolen-, Gadolein-, Eruca- oder Hypogäasäure ist.

16. Zusammensetzung nach einem der Ansprüche 11 bis 15, bei der der Glycerinmonoester Glycerinmonooleat ist.

17. Zusammensetzung nach einem der Ansprüche 11 bis 16, bei der Komponente (B) ein Ethylen/ungesättigter Ester-Copolymer umfasst, bei dem der ungesättigte Ester von ungesättigtem Alkohol mit ge-

sättigter Carbonsäure ist.

18. Zusammensetzung nach einem der Ansprüche 11 bis 17, die zusätzlich als Coadditiv eine öllösliche polare Stickstoffverbindung mit einem oder mehreren Substituenten mit der Formel $-NR^1-$ umfasst, in der R^1 eine Kohlenwasserstoffgruppe mit 8 bis 40 Kohlenstoffatomen bedeutet, wobei die Substituenten oder einer oder mehrere der Substituenten gegebenenfalls in Form eines davon abgeleiteten Kations vorliegen. 5 10
19. Zusammensetzung nach Anspruch 11 oder einem der Ansprüche 13 bis 18 in Abhängigkeit von Anspruch 11, bei der das Treib- oder Brennstofföl Mitteldestillattreib- oder -brennstofföl ist. 15
20. Zusammensetzung nach Anspruch 11 oder einem der Ansprüche 13 bis 19, in Abhängigkeit von Anspruch 11, bei der die Gesamtkonzentration der Komponenten (A) und (B) in dem Treib- oder Brennstofföl im Bereich von 25 bis 500 Gew.ppm aktiver Bestandteil je Gewichtsteil Treib- oder Brennstofföl liegt. 20 25
21. Verfahren zum Mischen von Additiven mit Treib- oder Brennstofföl, bei dem
 - (i) Komponente (B) gemäß der Definition in Anspruch 1 in das Treib- oder Brennstofföl injiziert wird, 30
 - (ii) Komponente (A) gemäß der Definition in Anspruch 1 in das Treib- oder Brennstofföl injiziert wird,
 - (iii) die Kaltfließigenschaften des Treib- oder Brennstofföls nach den Injektionen der Stufen (i) und (ii) gemessen werden, und 35
 - (iv) die relativen Injektionsraten von Komponente (B) und (A) und dadurch ihre relativen Mengen eingestellt werden, um die Resultate von Stufe (iii) zu berücksichtigen und die gewünschten Kaltfließigenschaften in dem Treib- oder Brennstofföl zu liefern. 40
22. Verfahren nach Anspruch 21, bei dem das Treib- oder Brennstofföl einen fließenden Strom desselben umfasst, Stufe (i) in einer ersten Station und Stufe (ii) in einer zweiten Station stattfindet. 45
23. Verfahren nach Anspruch 21 oder 22, bei dem ein Sensor die Stufe (iii) durchführt und die Information über eine Steuereinheit eingespeist wird, um die Injektion von einer oder beiden Komponenten (B) und (A) zu steuern. 50 55

Revendications

1. Utilisation d'un co-additif (A) qui comprend un additif d'onctuosité, soluble dans l'huile, comprenant un mono-ester de glycérol d'un acide monocarboxylique insaturé, dans lequel l'acide a 2 à 50 atomes de carbone ; ladite utilisation consistant en une utilisation dans une composition comprenant une proportion dominante d'un fuel-oil et une petite proportion d'un constituant (B) qui comprend un additif améliorant l'écoulement à froid comprenant un copolymère éthylène/ester insaturé ayant une moyenne en nombre du poids moléculaire mesurée par osmométrie en phase vapeur, de 1000 à 5000, et étant destiné à améliorer les propriétés d'écoulement à froid de la composition.
2. Utilisation suivant la revendication 1, dans laquelle l'additif d'onctuosité comprend l'ester d'un acide monocarboxylique de formule :

$$R'(COOH)$$
 dans laquelle R' représente un groupe alcényle ayant 10 à 30 atomes de carbone. 25
3. Utilisation suivant la revendication 2, dans laquelle le groupe alcényle a une, deux ou trois doubles liaisons.
4. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle l'acide est l'acide oléique, élaïdique, palmitoléique, pétrosélinique, ricinoléique, éléostéarique, linoléique, linoléinique, gadoléique, érucique ou hypogaéique.
5. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle le monoester de glycérol consiste en mono-oléate de glycérol.
6. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle le constituant (B) comprend un copolymère éthylène/ester insaturé.
7. Utilisation suivant la revendication 6, dans laquelle l'ester insaturé est un ester d'un alcool insaturé avec un acide carboxylique saturé.
8. Utilisation suivant l'une quelconque des revendications précédentes, comprenant en outre, comme co-additif, un composé azoté polaire, soluble dans l'huile, portant un ou plusieurs substituants de formule $-NR^1-$, dans laquelle R^1 représente un groupe hydrocarbyle contenant 8 à 40 atomes de carbone, ledit substituant ou bien un ou plusieurs desdits substituants étant facultativement sous forme d'un cation qui en est dérivé. 50 55

9. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle le fuel-oil consiste en un fuel-oil distillé moyen.

10. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle la concentration totale des constituants (A) et (B) dans le fuel-oil est comprise dans l'intervalle de 25 à 500 ppm d'ingrédient actif en poids, par poids du fuel-oil.

11. Composition de fuel-oil comprenant une proportion dominante d'un fuel-oil et une association :

d'un constituant (A) qui comprend un additif d'onctuosité, soluble dans l'huile, comprenant un mono-ester de glycérol d'un acide monocarboxylique insaturé, dans lequel l'acide a 2 à 50 atomes de carbone ; et

d'un constituant (B) qui comprend un additif améliorant l'écoulement à froid, comprenant un copolymère éthylène/ester insaturé ayant une moyenne en nombre du poids moléculaire mesurée par osmométrie en phase vapeur, de 1000 à 5000 ; et facultativement, d'autres additifs.

12. Concentré d'additifs contenant :

un constituant (A) qui comprend un additif d'onctuosité, soluble dans l'huile, comprenant un ester de glycérol d'un acide monocarboxylique insaturé, dans lequel l'acide a 2 à 50 atomes de carbone ; et

un constituant (B) qui comprend un additif améliorant l'écoulement à froid, comprenant un copolymère éthylène/ester insaturé ayant une moyenne en nombre du poids moléculaire mesurée par osmométrie en phase vapeur, de 1000 à 5000 ; et facultativement, d'autres additifs.

13. Composition suivant la revendication 11 ou 12, dans laquelle l'additif d'onctuosité comprend l'ester d'un acide monocarboxylique de formule :



dans laquelle R' représente un groupe alcényle ayant 10 à 30 atomes de carbone.

14. Composition suivant la revendication 13, dans laquelle le groupe alcényle a une, deux ou trois doubles liaisons.

15. Composition suivant la revendication 11 à 14, dans laquelle l'acide est l'acide oléique, élaïdique, palmitoléique, pétrosélinique, ricinoléique, éléostéari-

que, linoléique, linolénique, gadoléique, érucique ou hypogaeïque.

16. Composition suivant l'une quelconque des revendications 11 à 15, dans laquelle le monoester de glycérol consiste en mono-oléate de glycérol.

17. Composition suivant l'une quelconque des revendications 11 à 16, dans laquelle le constituant (B) comprend un copolymère éthylène/ester insaturé, dans lequel l'ester insaturé est un ester d'un alcool insaturé avec un acide carboxylique saturé.

18. Composition suivant l'une quelconque des revendications 11 à 17, comprenant en outre, comme co-additif, un composé azoté polaire, soluble dans l'huile, portant un ou plusieurs substituants de formule $-\text{NR}^1$, dans laquelle R^1 représente un groupe hydrocarbyle contenant 8 à 40 atomes de carbone, ledit substituant ou bien un ou plusieurs desdits substituants étant facultativement sous forme d'un cation qui en est dérivé.

19. Composition suivant la revendication 11, ou suivant l'une quelconque des revendications 13 à 18 lorsqu'elles dépendent de la revendication 11, dans laquelle le fuel-oil est un fuel-oil distillé moyen.

20. Composition suivant la revendication 11, ou suivant l'une quelconque des revendications 13 à 19 lorsqu'elles dépendent de la revendication 11, dans laquelle la concentration totale de constituants (A) et (B) dans le fuel-oil est comprise dans l'intervalle de 25 à 500 ppm d'ingrédient actif en poids, par poids de fuel-oil.

21. Procédé pour mélanger des additifs à un fuel-oil, comprenant les étapes consistant :

(i) à injecter le constituant (B) répondant à la définition suivant la revendication 1 dans le fuel-oil ;

(ii) à injecter le constituant (A) répondant à la définition suivant la revendication 1 dans le fuel-oil ;

(iii) à mesurer les propriétés d'écoulement à froid du fuel-oil après les injections des étapes (i) et (ii) ; et

(iv) à ajuster les vitesses relatives d'injection des constituants (B) et (A) et, ainsi, leurs proportions relatives pour tenir compte des résultats de l'étape (iii) et conférer les propriétés désirées d'écoulement à froid au fuel-oil.

22. Procédé suivant la revendication 21, dans lequel le fuel-oil comprend un courant en mouvement de ce fuel-oil, l'étape (i) s'effectuant à un premier poste et l'étape (ii) s'effectuant à un second poste.

23. Procédé suivant la revendication 21 ou 22, dans lequel un capteur met en oeuvre l'étape (iii) et l'information est amenée par un régulateur pour commander l'injection de l'un des ou des deux constituants (B) et (A).

5

10

15

20

25

30

35

40

45

50

55